NUCLEAR MAGNETISM AS SPACE REFERENCE

Murray J. Neufeld

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NUCLEAR MAGNETISM AS SPACE REFERENCE

by

Murray J. Neufeld

B.S., College of the City of New York, 1953

SUBMITTED IN PARTIAL FULFILLMENT OF THE

REQUIREMENTS FOR THE DEGREE OF

MASTER OF SCIENCE

at the

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

1955

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NUCLEAR MAGNETISM AS SPACE REFERENCE

by

Murray J. Neufeld

Submitted to the Department of Aeronautical Engineering on May 20, 1955 in partial fulfillment of the requirements for the degree of Master of Science.

ABSTRACT

An investigation of the principles of nuclear magnetic resonance absorption has been undertaken with emphasis on the associated relaxation mechanism of the nucleus. It was learned that in materials where the energy coupling between the spin system and the surrounding lattice structure is small, the energy of the spin system and hence of the associated intrinsic angular momentum vector direction is conserved for a period of time comparable to that of the relaxation time. Relaxation times of hours have been shown to exist in some materials. However, results of this study indicate that the direction of the angular momentum vector of the precessing nuclei is conserved principally with respect to the external magnetic field direction and not primarily with respect to inertial space.

Thesis Supervisor: Walter Wrigley

Title: Associate Professor of Aeronautical Engineering

28283

May 20, 1955

Professor Leicester F. Hamilton
Secretary of the Faculty
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Dear Professor Hamilton:

In accordance with the regulations of the faculty, I hereby submit a thesis entitled Nuclear Magnetism as Space Reference in partial fulfillment of the requirements for the degree of Master of Science without specification.

ACKNOWLEDGEMENT

The author expresses his appreciation to the personnel of the Instrumentation Laboratory, Massachusetts Institute of Technology, who assisted in the preparation of this thesis. Particular thanks are due to Dr. Claude Emmerich, who, as immediate supervisor, inspired and guided the entire project, to Dr. Elmer Frey for his interest and encouragement and to Professor John Waugh of the Chemistry. Dept. at M.I.T. and Mr. Redfield of the Harvard University Dept. of Physics for their help in the theoretical aspects of the problem. Special thanks to Mrs. Joan Fitzpatrick for her patience and typing.

The graduate work for which this thesis is a partial requirement was performed while the author was assigned to the U.S. Navy Training School, Massachusetts Institute of Technology. The thesis was prepared under the auspices of D.I.C. Project 7243 sponsored by the Aeronautical Research Laboratory of the Wright Development Center through U.S.A.F. Contract AF-33(616)-2392.

TABLE OF CONTENTS

OBJECT

The object of this thesis is to investigate the magnetic moment of a nucleus and its subsequent motion and orientation in the presence of magnetic fields and to determine as far as possible whether the principles involved may lead to a feasible solution to the problem of acquiring a reliable reference in inertial space.

CHAPTER 1

INTRODUCTION

It may be safely stated that a vital element in a self-contained inertial guidance system or motion isolation system is the gyroscopic element. For it is this element which provides the system with a vector position in inertial space* and which is used as a reference for the measuring instruments.

The theory of the gyroscope and its subsequent instrumentation and incorporation in various guidance and base motion isolation systems has been documented in the reports issued by the Instrumentation Laboratory at M.I.T. and need not be considered further. (See Appendix B)

It should be pointed out, however, that the very characteristics of nature which allow one to use the angular momentum vector as a space reference direction in a system, also render the system subject to interferences either natural or man-made, hence, the system can only be as good as the reliability of the angular momentum vector as a reference.

Despite the great reduction of bearing-friction torques by the

* Inertial space is the space in which Newton's Law of Inertia is valid, that is, the reference frame in which a force-free body is unaccelerated.

use of single degree of freedom floated gyro packages, the residual uncertainty torques which cause a drift rate in the angular momentum reference vector are of an order of magnitude large enough to cause concern in the resulting inaccuracies in the inertial navigation systems.

One approach to this problem is to make a detailed study of the effects of drift in inertial references[1]** another, is to analyze the frequency content of the actual minute detrimental disturbances[2] which the inertial system experiences while in operation. These two approaches have been and are being made at the Instrumentation Laboratory at M.I.T.. They both point to the need for a refinement of the existing gyroscope or at least for a good compensating device to cancel the detrimental effects to the extent that the causes of the disturbing torques are known.

Another approach is to search through other natural phenomena and see whether vector quantities can be found whose orientation is little or not at all affected by frictional forces or translational accelerations. The magnetic moment of a nucleus and its subsequent motion and orientation in the presence of external magnetic fields have caused enough interest to warrant a rather detailed study of the principles involved in order to determine, as far as possible, whether these principles may lead to a feasible solution to the problem of acquiring a reliable reference position in inertial space.

The most striking effects of nuclear magnetic phenomena have been revealed in experiments described by such various names as

** See bibliography in Appendix D for references in parenthesis.

nuclear resonance induction, nuclear resonance absorption, or radio spectroscopy, but they all illustrate the same principle.

The major purpose of this paper is to attempt to study the causes and effects of a precessing nuclear magnetic vector in the presence of external magnetic fields with some emphasis on the relaxation mechanisms associated with these motions.

The understanding of the magnetic properties of the nucleus is based on the supposition that the nucleus is, in general, a small magnet whose interactions with the atomic electrons split the energy levels between which the electrons make the transitions responsible for atomic line spectra. With the development of spectroscopic equipment, it ultimately became possible to determine certain nuclear spins and to measure a number of nuclear magnetic moments to about two significant figures.[3]

Considerably more accurate measurements were obtained in molecular beam experiments;[4][5] which were pioneered under O. Stern and later expanded by Rabi at Columbia University. An outstanding addition to beam technique was the magnetic resonance method,[6][7] which the Rabi group applied to these experiments. The most recent developments in the study of nuclear magnetic moments have applied the magnetic resonance principle to solids, liquids and gases in their normal physical states, and the compilation of data concerning nuclear magnetism has become even more rapid.

The new resonance techniques devised simultaneously and independently by the Purcell and Pound group[8][9] at Harvard and the Bloch and Hansen group[10][11] at Stanford, require simpler equipment

than do the beam experiments. Further, the new methods seldom require the alteration of the physical or chemical form of the sample containing the nucleus whose magnetic properties are to be studied.

The important phenomenon to be considered in magnetic resonance is the change of orientation of nuclear moments. His acquaintance with radio techniques during the war suggested to Bloch a way of detecting a reorientation of nuclear moments through the normal methods of radio reception. The signals to be detected would be due to the electromagnetic induction caused by nuclear reorientation and should appear as a voltage difference between the terminals of an external electric circuit.

In order to understand this principle, one can start from macroscopic quantities and describe the underlying phenomenon in simplified classical terms. Consider for this purpose, as a typical example, about one cubic centimeter of water with the protons contained in it as the nuclei under investigation. Their magnetic moments are oriented in a completely random manner in the absence of an external magnetic field. After the sample has been brought into such a field, however, there will be established a new thermal equilibrium in which the magnetic moments are distributed with a slight surplus parallel to the magnetic field. Even in relatively strong fields of the order of 10,000 gauss this surplus will, at room temperature, amount to no more than about one part in a million. While its direct observation would be difficult, there exists a "nuclear paramagnetism" in the sense that one deals with a finite macroscopic nuclear polarization which is both parallel and proportional to the applied external magnetic field. The establishment of thermal equilibrium demands the

transfer of the energy released by the partial orientation of the nuclear moments into heat, and this can take place only through interaction of these moments with their molecular surroundings. The strength of this interaction determines the time interval required for the nuclear moments to adjust themselves to the equilibrium conditions; it is measured by the "relaxation time", as in the analogous case of atomic paramagnetism. The role of relaxation is of basic significance and a more thorough discussion will be given later. For the moment, to describe the nuclear polarization under the conditions of magnetic resonance, let it be assumed that equilibrium conditions have been established. A simple mechanical consideration of the gyroscope shows that an alternating field at right angles to the constant magnetic field has the effect of tilting the direction of the polarization with respect to the constant field, and that the polarization will thereupon perform a precessional rotation about the field. The angular frequency of precession is proportional to the field with a constant of proportionality which is called the "gyromagnetic ratio" of the nucleus and which is equal to the ratio of its magnetic moment to its intrinsic angular momentum. From a macroscopic point of view, one thus deals with a situation in which the protons in the cubic centimeter of water have the effect of an invisible compass needle rotating in its interior. (See Fig. 1). The "invisibility" refers actually only to observation of optical frequencies; the rotation occurs in the range of radiofrequencies, and it can very well be observed by using Faraday's Law of Induction. (See Fig. 2). Indeed, the rotation of this "compass needle" is accompanied by that of a magnetic field which possesses an alternating component perpendicular to the

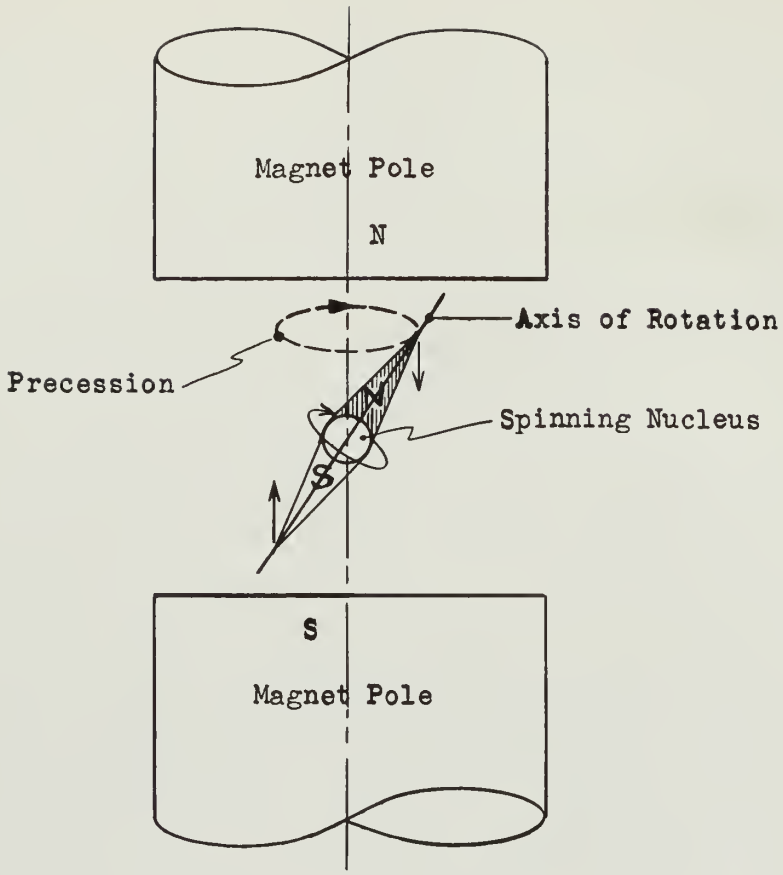


Fig. 1 Principal elements of nuclear precession. The drawing illustrates the precession of a nucleus in an external magnetic field. The torque arising from the action of the magnet upon the magnetic moment of the nucleus, which is symbolized by a compass needle, causes the magnetic moment vector to precess about the direction of the external magnetic field.

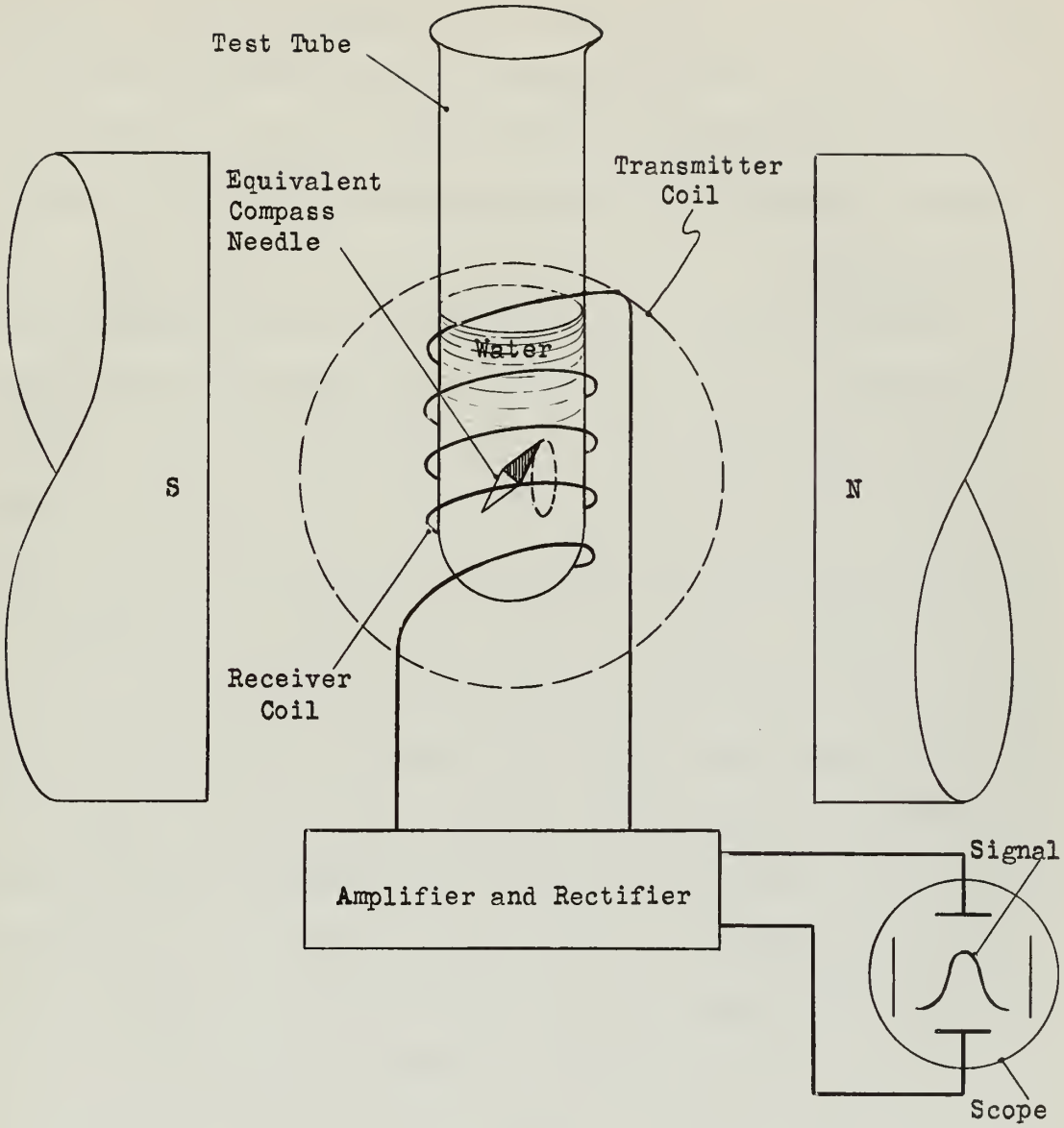


Fig.2 Schematic representation of induced nuclear signal. Under the influence of the field in the gap between the pole faces, the water in the test tube undergoes a slight nuclear magnetization and behaves in this respect like an equivalent compass needle, symbolically indicated in its interior. The adjoining small dotted curve represents the precession of this equivalent compass needle, occuring at the same rate as that of an individual nucleus. It causes an induced alternating voltage in the receiver coil, wound around the sample. After amplification and rectification, this voltage is displayed as a signal on the screen of the cathode-ray oscillograph.

axis of rotation, and hence is accompanied by an electromotive force, induced in a suitably wound coil of wire around the sample. From here it is a matter of standard techniques of radio reception to rectify and amplify this electromotive force so that it can be recorded on a voltmeter, displayed on a cathode ray oscillograph, or made audible in a loudspeaker.

Using the analogy of mechanical resonance the mechanism of relaxation can be seen to resemble friction. It counteracts the tilt produced by the alternating field. If the friction is large, i.e., if the relaxation time is short, it will either reduce the effect for a given amplitude of the alternating field or require a correspondingly larger amplitude. It will, in either case, result in a relatively broad resonance line, thus dimishing the accuracy of the measurement. Since the width of the resonance line determines the accuracy with which magnetic moments can be determined, the necessary conditions for obtaining sharp lines will be briefly considered. In the first place, it is necessary that the constant field has the same value in all parts of the sample; in the second place, in the induction type of experiment one must not choose an excessive amplitude of the alternating field, since this too would cause an excessive broadening. The ultimate limit is given by the natural width of the line, and it is closely related to the relaxation time. It can be seen, in fact, that theoretically the accuracy of a measurement by nuclear induction is limited only by the number of cycles through which the nuclear polarization vector rotates in its precession about the constant field during the relaxation time. As an example, we shall consider protons in pure water in a field of 10,000 gauss. The frequency of precession

here is 42.5 megacycles per second, so that about 10^8 cycles are performed during the relaxation time of approximately two seconds. This means that an accuracy of one part in 100 million could be achieved here in principle provided that a sufficiently homogeneous field were available. Although this limit has not yet been reached, it is noteworthy that in water, alcohol and other liquids, resolutions of one part in 10 million have actually been achieved. It is indeed the possibility of coherent observation over a large number of cycles which allows the use of nuclear induction as a method of high precision measurements.

In the ensuing chapters the concepts of magnetic resonance will be approached from two points of view:

(a) The resonance phenomena will be studied from a "microscopic" point of view, that is, the phenomena will be considered in terms of the individual nucleus. This treatment implies the use of results gleaned from quantum mechanical considerations. Where it is necessary, such results will be used without attempts at rigorous justification. However, plausibility arguments will be attempted in some instances where a clearer intuitive concept is desired.

(b) The resonance will also be studied from a "macroscopic" point of view, that is, the effects of resonance on a great number of nuclei will be treated by classical methods. This treatment is made possible through the use of the famous Bloch formulation.[10][11]

Although no new ideas on the concepts of nuclear magnetic resonance are presented in the following chapters the writer can best justify the desirability of this paper by quoting from a most distinguished

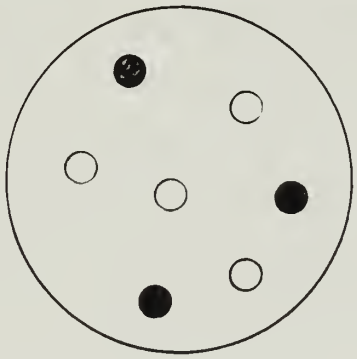
contributor to the fund of scientific knowledge.

> "There are .... some minds which can go on contemplating with satisfaction pure quantities presented to the eye by symbols, and to the mind in a form which none but mathematicians can conceive."
>
> "There are others who feel more enjoyment in following geometrical forms which they draw on paper, or build up in the empty space before them."
>
> "Others again are not content unless they can project their whole physical energies in to the scene which they conjure up. They learn at what rate the planets rush through space, and they experience a delighted feeling of exhiliration. They calculate the forces with which the heavenly bodies pull on one another, and they feel their own muscles straining with the effort."
>
> "To such men, momentum, energy, mass are not abstract expressions of the results of scientific inquiry. They are words of power, which stir their souls like memories of childhood."
>
> "For the sake of persons of these different types, scientific truth should be presented in different forms, and should be regarded as equally scientific whether it appears in the robust form and vivid coloring of a physical illustration, or in the tenuity and paleness of a symbolic expression." ..... James Clerk Maxwell(12)

CHAPTER 2

MAGNETIC AND ANGULAR MOMENTUM PROPERTIES OF THE NUCLEUS

The nucleus is composed of several particles called nucleons. Two kinds of nucleons are definitely known: the proton, with a mass about two thousand times larger than that of the electron and carrying a positive electric charge; and the neutron with a mass almost equal to that of the proton mass but electrically neutral. These particles must be thought of as undergoing a rapid motion within a narrow region of space schematically indicated by the surrounding circle of Fig.(3). The details of this motion remain to be investigated,



Approximate Scale

● Proton

○ Neutron

10^{-13} cm

Fig. 3 Schematic presentation of a nucleus. Neutrons and protons must both be thought of in a state of rapid motion, confined within a region which is indicated by the outer circle.

but one of its features is well known and is of primary importance at this point. Whatever the paths of the individual nucleons may be, it appears that in about half of the known nuclei, there exists a rotation of the nucleus as a whole about an axis, which passes through its center of gravity.

As a rotating mass the nucleus possesses the property of an angular momentum, directed along the axis of rotation. According to the laws of quantum mechanics, the magnitude of this angular momentum can only assume the values of (0, 1/2, 1, 3/2, etc.) $h/2\pi$, where h is Planck's quantum of action and where the bracketed values indicate the "Spin" of the nucleus. For all values of the spin different from zero, i.e., in all cases where a finite rotation exists, there exists another property of the nucleus. This other property arises from the fact that not only the masses but also the electrical charges located in the nucleus participate in the rotation. This rotation of the charges, similar to the circulation of the electrons in the atom, is equivalent to an amperian current so that the nucleus likewise can be expected to have the properties of an elementary magnet.

Thus, in addition to its well known properties of mass, charge and intrinsic angular momentum (spin), the atomic nucleus possesses in general a magnetic moment, that is, it behaves much as if it were a bar magnet. Although elementary textbooks often define the magnetic moment of a magnet as the product of its magnetic pole strength and the distance between its two poles, physicists believe that free magnetic poles do not exist and that a more accurate picture involves circulating electric currents or "current whirls". The magnetism of a bar of iron is attributed to "current whirls" of a kind within

the iron atoms, and similarly the magnetism of the nucleus may be considered as originating with circulating currents in the nucleus.

It would seem from the above description that the motion of the nucleons is a necessary requirement for the existence of a nuclear magnetic moment and that a proton at rest could not contribute to the magnetic moment of a nucleus. Actually that is not the case, since the proton itself is known to possess a spin of 1/2 and a magnetic moment. This "intrinsic" spin of an elementary particle may in some respects be thought of as a rotation about an axis which passes through the particle itself, somewhat analogous to the daily rotation of the earth. There is not much known, at present, about the corresponding amperian currents which evidently circulate within the particle and thus give rise to its intrinsic magnetic moment. The somewhat peculiar origin of the intrinsic magnetic moment of the particle is emphasized by the fact that the neutron, besides having a spin of 1/2, likewise exhibits a magnetic moment in spite of the fact that it carries no total electric charge. A quantitative understanding of nuclear magnetic moments requires that the intrinsic moments of the nucleons be taken into consideration. Furthermore, hydrogen, the simplest atom, has a nucleus which consists of a single proton so that in this case all the properties of the nucleus arise from the intrinsic spin and magnetic moment of a nucleon. The nucleus of the hydrogen atom is of particular interest since a great deal of the study of nuclear magnetism has, until recently, been carried out on matter containing hydrogen, i.e.,proton resonance.

Since the existence of an intrinsic angular momentum of the nucleus implies a circulation of mass within it, it should not be

surprising that the magnetic moment and angular momentum are related to each other. Indeed, classical models of the nucleus predict that these two vectors should be collinear and that their lengths should always be in the same ratio. For example, if one computes the magnetic moment of a spinning spherical shell with a charge q and mass M uniformly distributed over its surface, the magnetic moment obtained is:

$$\bar{\mu} = \frac{q}{2Mc}\,\bar{p} \tag{1}$$

where $\bar{p}$ is the angular momentum of the spinning shell and c is a constant numerically equal to the velocity of light in free space.

It will be shown that the nucleus does not conform accurately to this model, and that the resonance absorption phenomenon to be discussed provides one of the experimental methods for learning the relation between the nuclear magnetic moment and the vector $\bar{p}$. However, nuclear magnets differ only in magnitude and/or sign from the prediction of Eq.(1) and it can be shown that:

$$\bar{\mu} = g\,\frac{e}{2Mc}\,\bar{p} \tag{2}$$

where g is a number characteristic of a given nuclear species in a given nuclear energy state. The symbol M denotes the proton mass and e the proton charge.

Since the nuclear moment is proportional to the intrinsic angular momentum or "spin" of the nucleus, it is worthwhile to review the special properties of this vector according to modern physics. The angular momentum of any particle or system of particles is found to be

expressible in terms of a fundamental unit $\hbar$ (read h-bar) which is Planck's constant divided by 2π. The quantity usually denoted the "spin" is defined as $1/\hbar$ times the largest observable value of the time average of a component of $\bar{p}$ in a given direction. The direction of interest here will be the direction of an applied magnetic field $\bar{H}$ thus:

$$\text{"the spin"} = \left(\frac{1}{\hbar}\right)\left(p_H\right)_{max} = I \quad . \tag{3}$$

It is found experimentally and theoretically that the nuclear spin quantum number I can have integral or half-integral values. Each nuclear ground state is characterized by just one value of I.

A general expression for all the permitted values of p_H is:

$$p_H = m\hbar \tag{4}$$

where m = I, I-1, I-2, ..., -I+1, -I. Since quantum mechanical arguments show that the value of $\bar{p} \cdot \bar{p}$ is $I(I+1)\hbar^2$, the length of the angular momentum vector is:

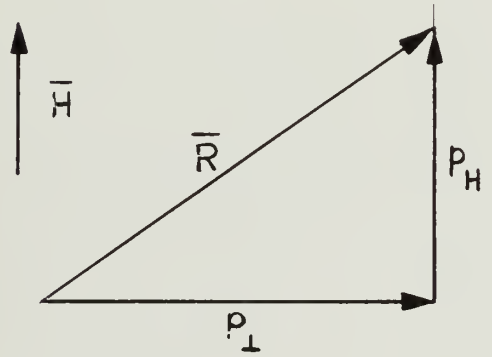
$$|\bar{p}| \quad \left[I(I+1)^{1/2}\right]\hbar \quad . \tag{5}$$

One can apply the relations to find the length of the component of $\bar{p}$ which is at right angles to the $\bar{H}$ - direction. Consider the proton which has been found experimentally to have I = 1/2. When $p_H = m\hbar$,

with m = + 1/2, the length of the vector is $|\bar{p}| = (\frac{\sqrt{3}}{2})\hbar$ and the perpendicular component is: (See Fig.4)

$$p_\perp = \left(\frac{\sqrt{2}}{2}\right)\hbar \tag{6}$$

which is even greater than (p_H) max. As I increases, (p_H) and $|\bar{p}|$ become more nearly equal. For an object which is massive (compared to a nucleus), such as a spinning baseball (p_H) max and $|\bar{p}|$ are for all practical purposes equal for measurable values of $\bar{p}$.



$$I = \tfrac{1}{2} \text{ for protons}$$

$$|\bar{p}| = \left[I(I+1)\right]^{1/2}\hbar = \frac{\sqrt{3}}{2}\hbar$$

$$p_H = m\hbar = \tfrac{1}{2}\hbar$$

$$|\bar{p}|^2 = p_H^2 + p_\perp^2$$

$$p_\perp = \left[|\bar{p}|^2 - p_H^2\right]^{1/2}$$

$$= \left[\tfrac{3}{4}\hbar^2 - \tfrac{1}{4}\hbar^2\right]^{1/2}$$

$$p_\perp = \frac{\sqrt{2}}{2}\hbar$$

Fig. 4 Vector components of the angular momentum $\bar{p}$ of the proton

The following paragraphs will discuss the concepts of Larmor precession and energy storage in a magnetic field.

If a magnet of dipole moment $\bar{\mu}$ is placed in a magnetic field $\bar{H}$, a torque $\bar{L}$, is exerted on the magnetic dipole, and in vector notation,

$$\bar{L} = \bar{\mu} \times \bar{H} \tag{7}$$

Newton's law of rotational motion states that the rate of change of angular momentum of a system is equal to the torque applied to it, or

$$\frac{d\bar{p}}{dt} = \bar{L} \tag{8}$$

Since the torque on a nucleus with magnetic moment $\bar{\mu}$ is given by Eq.(7) it follows that

$$\frac{d\bar{p}}{dt} = \bar{\mu} \times \bar{H} \tag{9}$$

However, since from Eq.(2), $\bar{\mu} = g(e/2Mc)\bar{p}$, we have

$$\frac{d\bar{p}}{dt} = -g\left(\frac{e}{2Mc}\right) \bar{H} \times \bar{p} \tag{10}$$

which is the equation of motion of the vector $\bar{p}$. The vector properties of Eq.(10) indicate that the magnitude of $\bar{p}$ is constant and that $\bar{p}$ is precessing with angular velocity

$$\omega_o = -g\left(\frac{e}{2Mc}\right) \bar{H} \tag{11}$$

To see this more clearly, note that in Fig.(5)

$$d\bar{p} = \bar{\omega}_0 \times \bar{p}\, dt \qquad (12)$$

gives the proper direction to d $\bar{p}$, as well as the proper magnitude.

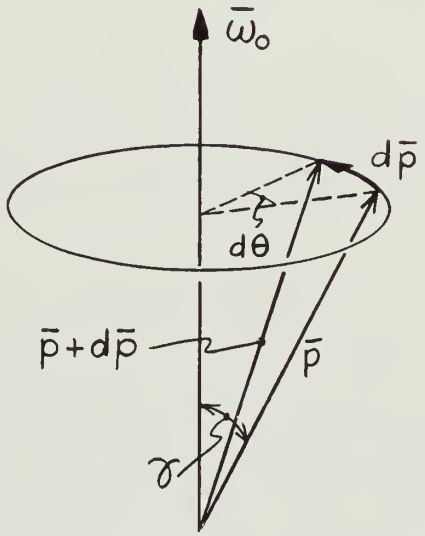


Fig. 5 Vector diagram used to illustrate the differential equation obeyed by a precessing angular momentum vector of constant magnitude.

Therefore, it may be concluded that if a nucleus of magnetic moment $\bar{\mu} = g\,(e/2Mc)\,\bar{p}$ is placed in a magnetic field, the magnetic moment vector (or the angular momentum vector) precesses with the angular frequency of Eq.(11) regardless of the angle between $\bar{\mu}$ and $\bar{H}$. This is called the "Larmor precession frequency".

Recalling Eqs.(1) & (5), it can be shown that the vector model of the nucleus may be described in terms of the magnetic moment as follows. The nuclear magnetic moment of a nucleus with spin I is a vector of length

$$|\bar{\mu}| = g\left(\frac{e}{2Mc}\right)\left[I(I+1)\right]^{1/2}\hbar \quad ; \tag{13}$$

it has a component

$$\mu_H = g\left(\frac{e\hbar}{2Mc}\right)m \quad , \qquad [m = I, I-1, \cdots, -I] \tag{14}$$

along the direction of an externally applied magnetic field $\bar{H}$, and a component of length

$$\mu_\perp = g\left(\frac{e\hbar}{2Mc}\right)\left[I(I+1)-m^2\right]^{1/2} \tag{15}$$

which is perpendicular to the external field and precesses with an angular frequency of magnitude

$$\omega_0 = g\left(\frac{e}{2Mc}\right)H \tag{16}$$

It may be shown from Eq.(7) that the potential energy U of a magnetic moment $\bar{\mu}$ in a magnetic field $\bar{H}$, except for an additive constant is

$$U = -\bar{\mu}\cdot\bar{H} = -\mu_H H \tag{17}$$

The energy associated with a nuclear dipole in a state characterized by m is (from Eqs.14 & 17)

$$U(m) = -g\left(\frac{e\hbar}{2Mc}\right) m H . \qquad (18)$$

A nucleus of spin I has, in general, (2I + 1) energy levels (one for each value of m) accessible to it in consequence of its interaction with a magnetic field $\bar{H}$. These are called Zeeman levels, inasmuch as they are similar to those responsible for the Zeeman line splittings in atomic spectra. It should be noted that the foregoing equations are valid whether g is negative or positive. The constant

$$\mu_0 = \frac{e\hbar}{2Mc} \qquad (19)$$

is called the nuclear magneton, and nuclear magnetic moments are often measured in terms of it. The "Bohr magneton", μ_β, which is the unit of measure for electronic moments, may be found from Eq.(19) by substituting the elctron mass for the proton mass. The value of the two magnetons are as follows:

$$\mu_0 = 5.049 \times 10^{-24} \frac{erg}{gauss}$$

$$\mu_\beta = 0.973 \times 10^{-20} \frac{erg}{gauss}$$

It is customary to let the vector $\bar{I}$ stand for the nuclear spin in units of $\hbar$. Then

$$\bar{I} \cdot \bar{I} = I(I+1)$$

$$I_H = m$$

These definitions can be combined to express most conveniently the nuclear magnetic moment as

$$\bar{\mu} = g \mu_0 \bar{I} \tag{20}$$

The quantity generally known as "the magnetic moment " is

$$(\mu_H)_{max} = gI\mu_0 \tag{21}$$

The dimensionless number gI is the "magnetic moment" measured in units of the nuclear magneton.

The effects of thermal agitation on an assembly of magnets are introduced by carrying out a simple derivation of the so-called static Curie susceptibility.

The magnetic induction, or magnetic flux density, within a sample of matter may be written as

$$\bar{B} = \bar{H} + 4\pi\bar{M} \tag{22}$$

Where $\bar{H}$ is the magnetic field and $\bar{M}$ is the volume density of magnetic dipole moments or the magnetic moment per unit volume of the sample.

In simple substances which are isotropic, the vector $\bar{M}$ is proportional to the applied magnetic field, as will be seen in the ensuing computation. The proportionality factor χ is defined as the magnetic susceptibility:

$$\bar{M} = \chi \bar{H} \tag{23}$$

Consider now a substance containing N nuclei per unit volume, and assume for simplicity their nuclear magnets are all alike. Since from Eq.(14), the value of the static magnetic moment component along the field direction is known for each state m, one can compute the magnetic moment per unit volume, $\bar{M}$, if the number of nuclei in each energy state were known. The natural tendency is for a magnet to align itself parallel to an external field, for, the potential energy is then a minimum. However, the thermal energy possessed by each degree of freedom of the nucleus by virtue of its temperature, T, is $\frac{1}{2} kT$, where k is the Boltzmann constant. A simple calculation shows that, even for the largest nuclear magnet, this thermal energy far exceeds the difference in energy between the parallel and the anti-parallel positions of the nuclear magnet in the field $\bar{H}$.

It is expected, therefore, that the collisions due to the thermal agitation in the sample will play such havoc among the ranks of the nuclear magnets, which the external field $\bar{H}$ seeks to align, that there will be but a very small excess of nuclei in the lowest energy state. To illustrate this effect quantitatively, the excess number of protons ($2I + 1 = 2$) in the lower energy state at room temperature

in a field of 20,000 gauss (usually the upper limit on fields obtainable in the laboratory) will be computed from the Boltzmann factor.

Let the number of nuclei per unit volume with energy U(m) be N(m). Then the ratio of the population of the two proton states m = 1/2 and m = -1/2 is, according to Boltzmann,

$$\frac{N(+\frac{1}{2})}{N(-\frac{1}{2})} = \frac{\exp\left[-U(\frac{1}{2})/kT\right]}{\exp\left[-U(-\frac{1}{2})/kT\right]} \simeq 1 + \mu_0 g \frac{H}{kT} \qquad (24)$$

since, at room temperature, $U(m) \ll kT$. Substituting the numbers H = 20,000 gauss, $kT = 4 \times 10^{-14}$ erg, and g = 5.58 for protons, one finds

$$\frac{N(+\frac{1}{2})}{N(-\frac{1}{2})} = 1 + 14.1 \times 10^{-6}$$

Thus, for every million nuclei in the upper energy state, there are one million and fourteen nulcei in the lower energy state. Clearly it is these fourteen protons in each two million which are responsible for the net nuclear magnetism of the sample.

While the value is small and would be difficult to observe directly, it is actually not the nuclear magnetism $\bar{M}$, but the rate of change of the rapidly varying nuclear induction $\bar{B} = 4\pi \bar{M}$, which is observed in the resonance experiments and which can be easily detected.

To compute the Curie susceptibility for any nucleus characterized by $\alpha = g\mu_0 H/kT$, the following sum is required

$$M_H = \sum_{m=-I}^{I} N(m)\mu_H(m) = K \sum_{m=-I}^{I} \exp\,[m\alpha]\, g\mu_0 m \qquad (25)$$

Since $\alpha \ll 1$, the constant K is evaluated from

$$N = \sum_{-I}^{I} N(m) = \sum_{-I}^{I} K \exp\,[m\alpha]$$

as N/(2I + 1). Thus Eq.(25) becomes

$$M_H = \frac{N}{2I+1} \sum_{-I}^{I} (H+\alpha m)\alpha \frac{kT}{H}\, m$$

$$M_H = \frac{N}{2I+1}\, \alpha^2 \frac{kT}{H} \sum_{-I}^{I} m^2 \qquad (26)$$

Whether I is integral or half-integral, it may be shown that

$$\sum_{-I}^{I} m^2 = \frac{1}{3}\, I(I+1)(2I+1)$$

and the final result is

$$M_H = \left(\frac{N}{3kT}\right) g^2 \mu_0^2\, I(I+1) \qquad (27)$$

A comparison of Eq.(27) with Eq.(23) identifies the Curie susceptibility, which is denoted by χ_0 :

$$\chi_0 = \left(\frac{N}{3kT}\right) g^2 \mu_0^2\, I\,(I+1) \qquad (28)$$

Returning to the example of the proton, it is seen that Eq.(28) gives the magnetic moment per unit volume arising from the fourteen excess protons aligned parallel to $\overline{H}$ out of every two million protons in the sample. With reduced temperatures, the excess population in the lower energy state increases. Indeed, at very low temperatures the nuclear effect becomes so pronounced as to be experimentally measurable; the static Curie susceptibility of solid hydrogen has been measured directly by Laserew and Schubnikow.[13]

CHAPTER 3

MAGNETIC RESONANCE

The results of Chapter 2 and the Bohr frequency condition can be used to conclude that nuclear resonance absorption may occur.

Bohr's explanation of the hydrogen spectrum involved the postulate that a system characterized by two discrete energy states separated by energy ΔU may make a transition from one state to the other accompanied by either emission or absorption of a quantum electromagnetic radiation of energy

$$\hbar\omega = \Delta U \tag{29}$$

Whether the quantum is emitted or absorbed is determined by energy conservation for the transition in question.

In Chapter 2, a nucleus in a magnetic field was shown to have $(2I + 1)$ energy levels accessible to it, and if $I \neq 0$, transitions are possible. The energy difference between any two such levels in a constant external magnetic field $\bar{H}_0$ is

$$U(m'') - U(m') = g\mu_0 H_0 (m' - m'') . \tag{30}$$

Only transitions in which m changes by + 1 or - 1 are permitted by a so-called "selection rule" and therefore transitions are permitted between adjacent states of an energy level scheme such as that of Fig. (6) which applies to a nucleus with I = 5/2.

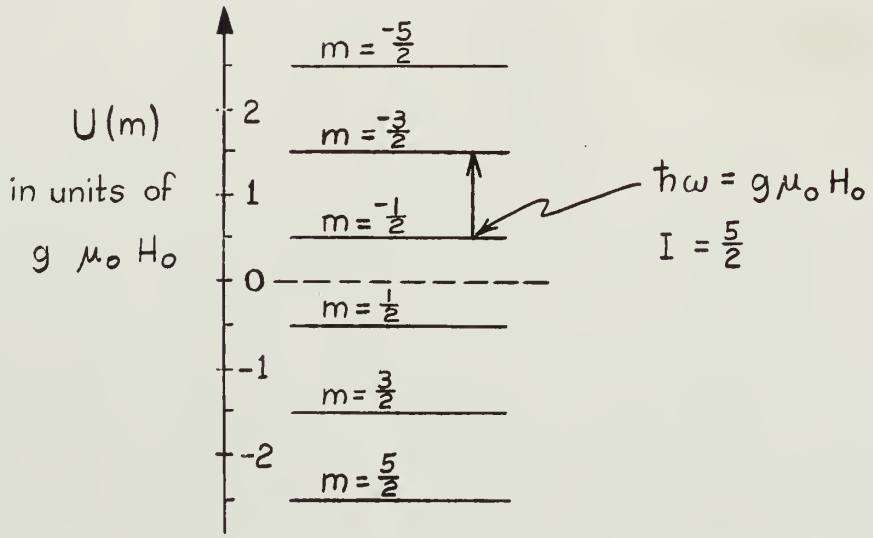


Fig. 6 Energy level diagram for a nuclear moment of spin 5/2, showing schematically the absorption of a quantum of radiation which induces a transition between a pair of adjacent Zeeman levels.

The selection rule applied to Eqs.(29) & (30) determines the frequency of the radiation emitted or absorbed by the nuclear magnetic dipole:

$$\hbar\omega_0 = g\mu_0 H_0 \quad ; \quad \omega_0 = \frac{g\mu_0}{\hbar} H_0 = \gamma H_0 \qquad (31)$$

which is precisely the Larmor frequency of Eq.(16). Protons in a field of 10,000 gauss precess at a frequency $\omega_0/2\pi = 42.6 \times 10^6$ sec^{-1}, which is in the radiofrequency range.

To summarize, if one subjects a sample containing nuclear magnets to radiation at the Larmor frequency, which is the order of megacycles in ordinary laboratory magnetic fields, a nucleus in a lower Zeeman

energy state may absorb a quantum of energy from the radiation field and make a transition to the next higher energy state. If the frequency of the radiation is not near the Larmor frequency, little or no absorption is expected, and hence the absorption is what physicists call a "resonance phenomenon".

This cursory argument ignores entirely a number of important details. For example, are there sufficient excesses of nuclei in the lower energy states for a measurable net absorbtion to occur? If so, what means exist to maintain this distribution during the absorption process? Are there any details about the radiation, such as its polarization, which are important? Some of these questions will be dealt with later.

At present, an attempt will be made to view with some detail the torques generated by an alternating magnetic field. Suppose that a small magnetic field $\bar{H}_1$ rotating with an angular frequency ω is in some way placed at right angles to the constant magnetic field $\bar{H}_0$, where $H_1 \ll H_0$. The additional field $\bar{H}_1$ will produce a new torque $\bar{L}_{flop}$ which tends to tip the vector $\bar{\mu}$. Note, however, that if H_1 rotates at a frequency appreciably different from the Larmor precession frequency of $\bar{\mu}$ in the large magnetic field, $\bar{L}_{flop}$ will change sense periodically with a frequency which is the difference between ω and ω_0. This is seen from Fig.(7) by noting that when $\bar{H}$ has the position OA with respect to $\bar{\mu}$, $\bar{L}_{flop}$ tends to tip $\bar{\mu}$ downward, but when $\bar{H}_1$ has position OB, its torque ($\bar{L}'_{flop}$) tends to tip $\bar{\mu}$ upward. This periodic change in sense of $\bar{L}_{flop}$ when ω and ω_0 differ appreciably leads to a zero time average for the flopping torque.

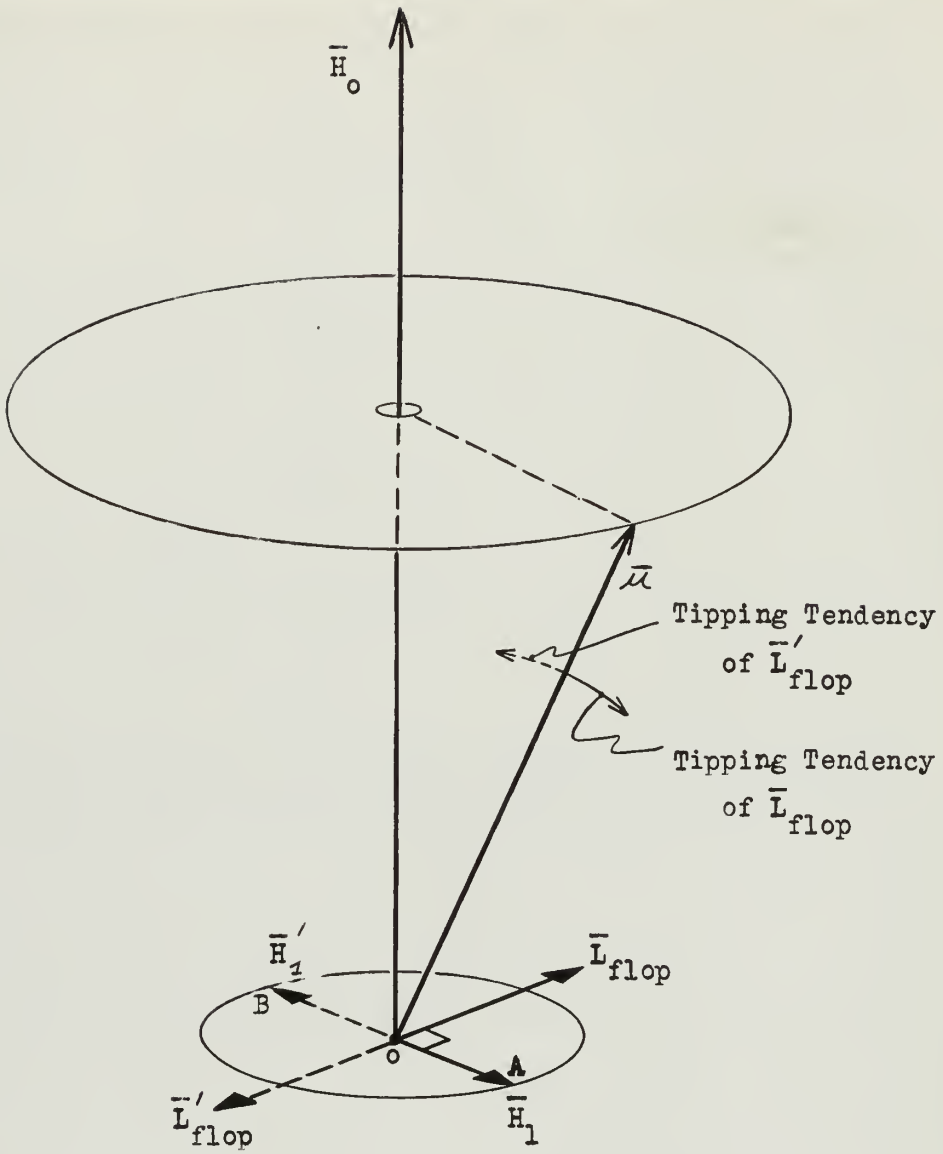


Fig. 7 Vector diagram illustrating the tendency of the small precessing magnetic field $\bar{H}_1$ to tip the magnetic moment vector as it precesses in a large constant field $\bar{H}_o$.

But when $\omega = \omega_0$, $\bar{L}_{flop}$ tends always to tip $\bar{\mu}$ in the same sense. If the vector $\bar{\mu}$ does tip and thus change its angle with respect to $\bar{H}_0$, energy must either be absorbed or emitted; hence again, one is led to the resonance condition, this time by purely classical considerations.

The magnetic field $\bar{H}_1$ must rotate with angular frequency ω_0, whereas it seems natural to think of the electromagnetic radiation mentioned at the beginning of this chapter as possessing an oscillatory magnetic component. The two points of view are reconcilable if one notes that an oscillatory field consists of two superimposed fields which rotate in opposite directions. Consider the field

$$\left.\begin{aligned} H_x &= 2H_1 \cos \omega t \\ H_y &= 0 \\ H_z &= 0 \end{aligned}\right\} \qquad (32)$$

This is expressible as the sum of two fields,

$$\left.\begin{aligned} H_x^{right} &= H_1 \cos \omega t \\ H_y^{right} &= H_1 \sin \omega t \\ H_z^{right} &= 0 \end{aligned}\right\} \qquad \left.\begin{aligned} H_x^{left} &= H_1 \cos \omega t \\ H_y^{left} &= -H_1 \sin \omega t \\ H_z^{left} &= 0 \end{aligned}\right\} \qquad (33)$$

which rotate about the z axis with frequency ω, but in opposite directions. If the oscillating field in Eq.(32) has $\omega = \omega_0$, one of its rotating components will follow the precessing vector $\bar{\mu}$ and

produce transitions as already discussed. The oppositely rotating component is far off resonance and its effect is negligible.

These considerations lead one to expect that the radiation which is to induce the transitions mentioned at the beginning of this chapter should be polarized with its magnetic vector at right angles to the large field $\bar{H}_0$.

The simple arguments of the above paragraphs attempt to make the absorption plausible, but a quantum mechanical treatment is required to establish firmly the properties of absorption by an assembly of nuclear magnets. Quantum mechanics does not give complete information with regard to the energy, angular momentum, and position of each nucleus at any time, but it does provide all that is necessary to know, namely, the probability that a nuclear magnetic moment initially in a state m will at some later time be found in a state m^1. This probability, expressed per unit time will be denoted by $P\ (m \longrightarrow m^1)$.

If a nucleus in one of its Zeeman energy states is immersed in a radiation field with energy in the frequency range $d\nu$ near ν given by $\rho(\nu)\,d\nu$, one expects the probability of a transition to be proportional to the number of quanta present with the frequency near the Larmor frequency, that is, proportional to $\rho(\nu_0)$. In fact the quantum mechanical result obtained by perturbation theory is

$$P\,(m \longrightarrow m') = \left(\frac{2\pi}{3\hbar^2}\right) g^2 \mu_0^2 \left|\bar{I}_{mm'}\right|^2 \rho(\nu_0) \qquad (34)$$

The quantity $\left|\bar{I}_{m\ m^1}\right|$ which is the so-called "matrix element" of the nuclear spin, is usually of the order of magnitude of unity; and when $|m^1 - m| > 1$ it vanishes, giving rise to the selection rule mentioned at the beginning of this chapter.

Consider an isolated magnetic moment with I = 1/2 (single proton) in a constant magnetic field $\bar{H}_0$ perpendicular to which is a precessing smaller field $\bar{H}_1$. Rabi[14] computed the transition probability directly from the Schrödinger equation containing the time, without resorting to perturbation theory. He found the chance C (1/2 ⟶ -1/2) for a nucleus initially in the state m = 1/2 to be at a later time t in the state m = 1/2 is

$$C\left(\tfrac{1}{2}\rightarrow -\tfrac{1}{2}\right)=\frac{\sin^2\theta}{1+(\omega_0/\omega)^2-2(\omega_0/\omega)\cos\theta}\ \sin^2\left\{\frac{\omega t}{2}\left[1+\left(\frac{\omega_0}{\omega}\right)^2-2\frac{\omega_0}{\omega}\cos\theta\right]^{1/2}\right\} \qquad (35)$$

Where tan θ = H_1/H_0. In this equation C is <u>not</u> a probability per unit time, but is rather the total probability at any time t. The sign of the ratio is negative if the rotation of $\bar{H}_1$ is not in the same sense as the nuclear precession. In most experiments $H_1 << H_0$ and Eq.(35) becomes

$$C\left(\tfrac{1}{2}\rightarrow -\tfrac{1}{2}\right)=\frac{\theta^2}{\left[1-\omega_0/\omega\right]^2+(\omega_0/\omega)\theta^2}\ \sin^2\left\{\frac{\omega t}{2}\left[\left(1-\frac{\omega_0}{\omega}\right)^2+\frac{\omega_0}{\omega}\theta^2\right]^{1/2}\right\} \qquad (36)$$

When resonance is obtained, that is, $\omega = \omega_0$, a value of t can be obtained for which C $(1/2 \longrightarrow -1/2)$ is as close to unity as one pleases. Moreover, when $\omega = -\omega_0$, C $(1/2 \longrightarrow -1/2)$ becomes extremely small confirming the conclusion made earlier that the wrong-rotating half of the oscillating field has a negligible effect.

At resonance, the expression, Eq.(36), oscillates between 0 and 1 as time progresses. This hints at a result which was explicitly found by Rabi and also by the perturbation treatment, namely,

$$C\left(\tfrac{1}{2} \longrightarrow -\tfrac{1}{2}\right) = C\left(-\tfrac{1}{2} \longrightarrow \tfrac{1}{2}\right)$$
$$P\left(\tfrac{1}{2} \longrightarrow -\tfrac{1}{2}\right) = P\left(-\tfrac{1}{2} \longrightarrow \tfrac{1}{2}\right) \qquad (37)$$

The classical discussion made this likely, for there is nothing about the rotating field $\bar{H}_1$ which will turn off $\bar{L}_{flop}$ after the magnetic moment $\bar{\mu}$ has been tipped to a new position with respect to $\bar{H}_0$ (and therefore, to a new energy).

Since the expression, Eq.(36), applies only to a single magnetic moment one must be careful in applying conclusions drawn from Eq.(36) to an assembly of interacting spins. First, as will be seen later, C $(1/2 \longrightarrow -1/2)$ becomes quite small if ω_0/ω differs from unity by even a very small amount, (this indicates a very narrow resonance line from the point of view of frequency changes). Then again, inhomogeneties in any laboratory magnetic field will make it impossible for a sizeable fraction of the nuclei initially in state m = 1/2 to have their C's near unity at any instant. Further, the nuclear magnets produce time varying local magnetic fields affecting their

neighbors which tend to spread ω_0 over an appreciable range. Only a small portion of these frequencies will be covered at any instant by a single monochromatic radiation source.

The equal probability found in Eq.(37) for transitions downward in energy (stimulated emission) and transitions upward in energy (absorption) emphasizes the following fact: If a net absorption is to occur, then at all times the excess number of nuclear magnets (14 per million) must remain in the lower energy state at equilibrium. Otherwise, every absorptive transition will be balanced, on the average, by an emissive transition, and there will be no net energy exchange.

One is thus faced with the problem: how is thermal equilibrium among spin states established, and, once established can it be maintained during a resonance experiment? These questions lead to the concepts of nuclear relaxation times or the rate of energy change between the spin system and the surrounding lattice structure. If the "coupling" between the spin system and lattice structure is small, i.e., if the relaxation time is long, then the energy of the spin system is conserved for a period as long as the relaxation time. This suggests the existence of a system which has a rotating magnetic moment and hence an associated angular momentum whose energy and therefore vector direction is conserved for a period long enough to be used as a reference. However, in the next chapter, a detailed study of the meaning of relaxation time and the method of conservation of energy will show that the practical realization of a reference utilizing this phenomenon will prove to be rather difficult.

CHAPTER 4

THE RELAXATION PROCESS

Consider a sample containing nuclear magnetic moments which resides initially in a small magnetic field such as that of the earth. The Boltzmann factors for the various Zeeman energy states are almost exactly unity and the spins are essentially equally distributed among the $2I + 1$ spin states. If this sample is thrust suddenly into the gap of an electromagnet which produces a field of 10,000 gauss, one asks how much time must elapse before the equilibrium excess number of nuclei will have found their way into the lower energy states. One is thus interested in the mechanism of the so-called relaxation process by which equilibrium is established. From a thermodynamic point of view, a relaxation process is thus any method of energy exchange between the system of nuclear spins and the lattice.

At the first instant after insertion into the magnetic field, and before equilibrium is obtained, the nuclear spins are still very nearly distributed in equal numbers among the $2I + 1$ levels. A study of Eq.(24) indicates that, since H_0 and therefore $U(m)$, is now large, the exponent can remain negligible only if the temperature T_s of the spin system is extremely high. In fact for $I = 1/2$, the excess number in the lower energy state defines at any time the spin temperature T_s.

Thus, the problem is one of describing the heat exchange between the lattice of vibrating atoms or molecules and the system of nuclear magnets, whose existence is usually well-sheltered by the enveloping electron closed-shells formed during the chemical combination which brought the lattice into being.

In order for the spins to "cool down", it is necessary that transitions from the upper spin states to the lower states occur more frequently than the reverse transitions. This seems, at first, to be incompatible with the result of Eq.(36) which shows that the probabilities in both directions are equal. However, the present situation differs from that considered in the previous chapter in that the entire system, consisting of lattice, radiation field, and spins, is being left to itself to come to equilibrium at a definite temperature, whereas the monochromatic radiation field of the previous chapter never comes to equilibrium with the nuclear spins at a common single temperature. Therefore, the probabilities of the previous chapter cannot be applied to the relaxation process without first taking into account certain properties and consequences of the equilibrium.

Let N(p) and N(q) be the equilibrium populations of two Zeeman levels p and q which differ in energy by $U_p - U_q$. Then a detailed balancing of the transitions between p and q will preserve equilibrium

$$N(p)\, W(p \rightarrow q) = N(q)\, W(q \dashrightarrow p) \qquad (38)$$

where $W(p \longrightarrow q)$ is the total probability per unit time of a single transition from p to q. But at equilibrium, the Boltzmann factor governs $N(p)/N(q)$ and

$$\frac{W(p \to q)}{W(q \to p)} = \frac{N(q)}{N(p)} = \exp\left(\frac{U_p - U_q}{kT}\right) \qquad (39)$$

The probability of a single transition from p to q cannot depend upon the population of q, and one must suppose that the total probabilities, W, are related to the quantum mechanical probabilities P through the Boltzmann factor of the final state, even when equilibrium has not yet been established; thus

$$W(p \longrightarrow q) = P(p \to q)\, \exp\left(\frac{-U_q}{kT}\right) \qquad (40)$$

To consider a case in detail, choose $I = 1/2$ and let the total number of spins be N, the population of the lower and upper energy states being repsectively $N(+)$ and $N(-)$. Then since $P(+ \longrightarrow -) = P(- \longrightarrow +) = P$ one obtains from Eqs.(40) & (30)

$$W(+ \longrightarrow -) = P \exp\left(-\frac{g \mu_0 H_0}{2kT}\right)$$

$$W(- \longrightarrow +) = P \exp\left(+\frac{g \mu_0 H_0}{2kT}\right) \qquad (41)$$

The excess number $n = N(+) - N(-)$ changes by 2 for each transition. This fact and the definition of the probabilities leads to the differential equation

$$\frac{dn}{dt} = 2N(-)W(-\rightarrow+) - 2N(+)W(+\rightarrow-) \quad (42)$$

Since $n << N$ for all cases of interest here, Eq.(40) may be written as

$$W(+\rightarrow-) = P\left[1 - \frac{|g|\mu_0 H_0}{2kT}\right]$$
$$W(-\rightarrow+) = P\left[1 + \frac{|g|\mu_0 H_0}{2kT}\right] \quad (43)$$

Substituting Eq.(43) into (42) yields

$$\frac{dn}{dt} = 2P(n_0 - n) \quad (44)$$

Where $n_0 = N\,|g|\mu_0\, H_0/kT$ is the equilibrium value of n. Integration of the above equation (44) yields

$$n = n_0\left[1 - exp\,(-2Pt)\right] \quad (45)$$

It should be noted that the equilibrium excess number is established in a fashion analogous to the charging of the capacitor of time constant 1/2P. This characteristic time

$$T_1 = \frac{1}{2P} \quad (46)$$

is called the spin-lattice relaxation time or the thermal relaxation time, or as Bloch calls it, the longitudinal relaxation time. This is the time required for all but 1/e of the equilibrium excess number of spins to reach the lower energy state.

Theories of nuclear relaxation must compute P from Eq.(34). Waller[14] made one of the pioneering attempts in this direction. He examined the effect of the spectrum of vibration and other lattice motions responsible for the specific heat of the solid. Such vibrations of the charged particles of the lattice lead to oscillatory currents and therefore to oscillatory local magnetic fields. The spectral intensity of these oscillatory local magnetic fields at the Larmor frequency should determine P according to Eq.(34). However, this mechanism leads to values of T_1 which are several orders of magnitude too large. Bloembergen, Purcell and Pound[8] have studied relaxation in fluids and found that Brownian motions at the Larmor frequency provide the relaxation mechanism.

Thermal relaxation times thus far measured range from 10^{-4} seconds or less in certain solutions containing paramagnetic ions to several hours for very pure ice crystal at liquid nitrogen temperatures. The value of T_1 for protons in water at room temperature has been measured by Hahn[15] to be 2.33 ± 0.07 seconds, in good agreement with the theory of Bloembergen, Purcell and Pound.[8]

For the sake of an intuitive concept of what is physically going on when the relaxation process is taking place, one may conjure up the following simplified mental picture. Consider the precession of a number of magnetic moment vectors immersed in a constant external magnetic field where the exciting fields at right angles to this

constant external field has been removed. Now from the point of view of conservation of energy, if there is no mechanism available to dissipate the energy associated with the motion of this spin system, then theoretically this motion should go on continuously. But there now exists a method of energy dissipation, namely, that of frequency coupling with the relatively distant lattice and molecular structure. If this lattice structure has the geometry and motion which permits a large rate of energy transfer between the spin system and lattice structure then the energy of the spin system will run down rapidly, i.e., short relaxation time. However, certain compounds are available (calcium fluoride, for example) where the "coupling" mentioned earlier is very weak and hence gives rise to long relaxation times (hours).

It was the intention at the outset of this investigation to utilize this long relaxation time as follows: Inasmuch as there is an angular momentum associated with the precessional motion and since the energy of this system is conserved over a long period of time, then perhaps one has available the equivalent of a bearingless, frictionless gyroscope. The direction of this angular momentum should, it would seem, be preserved for the length of the relaxation time. However, this is not the case, since as a result of this investigation the following has been ascertained: Although in the case of a long relaxation time, it is true that the energy of the spin system is conserved, it should be borne in mind that the system in which this energy resides consists of nuclear magnets plus the external constant magnetic field. Therefore, the resulting direction of the associated angular momentum vector is conserved only with respect to

the direction of the external magnetic field and not with respect to inertial space. Hence, unless the external field is stabilized with respect to inertial space, any physical rotation of the external field will cause the associated nuclear angular momentum to realign itself with the new direction of the external field.

The preceding paragraphs dealt with interactions between the system of nuclear spins and the lattice. In addition, each individual precessing nuclear magnet interacts with neighboring spins through their magnetic fields. In fact, the total magnetic field at any single nucleus consists not only of the applied field H_0, but includes also the resultant of the local fields produced by the static components of neighboring magnetic dipoles. Depending upon the arrangement of its neighbors among the $2I + 1$ values of μ_H, a given nucleus "sees" a slightly larger or slightly smaller field than that externally applied. One can estimate this effect by finding the magnitude of the local field which a nuclear magnetic dipole may be expected to produce at a distance of an angstrom unit or so.

$$H_{local} \sim \mu_0 r^{-3} \sim 5 \text{ gauss} \qquad (47)$$

One can expect a dispersion or spread of values of the precession frequency because of the variation of these several gauss of the effective magnetic field at different nuclei throughout the sample. The magnitude of the precession frequency spread, $\delta \omega_0$ is then

$$\delta\omega_0 \sim g\mu_0 \hbar^{-1} H_{loc} \sim 10^4 \text{ sec}^{-1}. \qquad (48)$$

One can interpret this as meaning that if two nuclei are known to be precessing in phase at time t = 0, they may be expected to have lost their phase relationship within a time the order of $1/\delta\omega_0 \sim 10^{-4}$ seconds.

A second process can occur to interrupt the phases of the precessing spins. If nuclei A and B are anti-parallel to each other, the precessing component of A's magnetic moment produces at B a precessing magnetic field at nearly the proper frequency to produce a transition and vice versa. It is therefore possible for A and B to flip each other over, leaving the net energy of the spin system unchanged. In effect, spins A and B have interchanged positions in the lattice, and this is often called a spin exchange or spin-spin collision.

Though the spin collision does not affect the total energy of the spin system, it does limit the lifetime of a spin state and leads, through the Heisenberg uncertainty relation, to an energy spread or dispersion. Since the relative phases of the two neighboring spins change appreciably during a time $1/\delta\omega_0$, one can expect that nucleus A will require a time of that order of magnitude before the Larmor frequency becomes precisely equal to that of spin B, and the lifetime of a spin state should be limited by spin-spin collisions to times the order of $1/\delta\omega_0$. Consequently the energy levels are broadened by an amount of δU given by

$$\delta U \cdot \left(\frac{1}{\delta \omega_0}\right) \sim \hbar \qquad (49)$$

In accordance with the Heisenberg uncertainty principle. One again arrives at the conclusion that the relative phases of the precessing nuclear spins will be destroyed over times the order of $1/\delta\omega_0 \sim 10^{-4}$ seconds, as a consequence of the interruption of a precessing state through spin-spin collisions.

The observable effect of these two phase destroying processes arises through the spread in energy levels, that is, the dispersion of Larmor frequencies, which imparts to the absorption line a finite width. This effect, therefore, decreases the accuracy of the measurement.

The quantum mechanical calculation of line width verifies that both local field dispersion and spin exchange are real effects which broaden the line. Reports by F. Bitter and N. L. Alpert[16] verify the fact that in solids the intermuclear fields tend to broaden the resonance lines. However, when the rotations within the sample occur with frequencies greater than the Larmor frequency involved, the intermuclear fields practically average out to zero during one Larmor cycle, thus resulting in a narrow line.

The time (10^{-4} seconds) referred to above is denoted as the "transverse relaxation time" and is symbolized by

$$T_2 = \frac{1}{\delta\omega_0} \sim 10^{-4} \text{ seconds} .$$

Thus far, the point of view has often been "microscopic", that is, the various phenomena have been considered in terms of the individual nucleus. This was done primarily to point out the inherent physical difficulties involved when one attempts to utilize these phenomena as a means to establish a vector reference with respect to inertial space.

It cannot be denied, however, that in the principle of nuclear magnetic resonance there exists a means of attaining a measurable quantity with a high degree of precision. The accuracy of this measurement is limited essentially by the degree of homogeneity attainable in a magnetic field. Hence, from the point of view of carrying out actual experiments where one deals with matter in bulk, it is the behavior of the "macroscopic" magnetic moment which becomes important. This leads to the next chapter and the classical approach to the famous Bloch formulation.

CHAPTER 5

THE CLASSICAL APPROACH OF BLOCH

The magnetic moment per unit volume, $\bar{M}$, of the experimental sample is related to the magnetic field $\bar{H}$ through the magnetic susceptibility χ, which is conveniently selected as the quantity to which the absorption will be related. As in the familiar example of the magnetic absorption which leads to hysteresis losses in a transformer core, the energy absorbed by a unit volume of the sample per second is

$$A = \frac{\omega}{2\pi} \int_{t=0}^{t=2\pi/\omega} \bar{H} \cdot d\bar{M} \,. \tag{50}$$

The integral itself represents the energy absorbed per cycle. It is convenient to represent the oscillatory magnetic field as the real part of a complex number

$$\mathcal{H} = 2H_1 \exp(i\omega t) \tag{51}$$

(Script letters are used to denote complex quantities.) The physi-

cally observable magnetization is the real part of the complex quantity $\mathcal{M}$ which is the product of the complex susceptibility $\chi = \chi' - i\chi''$ and $\mathcal{H}$:

$$M = \chi'(2H_1 \cos \omega t) + \chi''(2H_1 \sin \omega t). \qquad (52)$$

Since $2H_1$ cos wt is the applied field, the imaginary portion of the susceptibility is a measure of the out-of-phase component of magnetization.

If $\bar{M}$ and $d\bar{M}/dt$ are taken to be collinear with $2\bar{H}_1$, the integral (50) may be evaluated to yield

$$A = 2H_1^2 \omega \chi''. \qquad (53)$$

The energy absorbed by the nuclear spin system is therefore proportional to χ'', the out of phase component of the nuclear magnetization. In the following paragraphs the resonance properties of χ'' will be demonstrated, thereby establishing nuclear magnetic resonance absorption.

The equations of motion involving the nuclear magnetization $\bar{M}$ and the total magnetic field can be written from the discussion of earlier chapters. These equations were set up and solved by Bloch,[11] who sought a phenomenological description of the nulcear induction effect which is closely related to the absorption treated here.

Let the sample be placed in a large constant magnetic field $\bar{H}_0$ which lies along the z axis of a rectangular coordinate system, and suppose a small magnetic field to precess about the z axis. Then

the magnetic field vector is to include $\bar{H}_0$ and the "left" rotating portion of Eq.(33)

$$\left.\begin{aligned} H_x &= H_1 \cos \omega t \\ H_y &= -H_1 \sin \omega t \\ H_z &= H_o \end{aligned}\right\} . \qquad (54)$$

The rotating field has its angular velocity vector along the direction of $-z$ because Eq.(11) indicates that a positive magnetic moment precesses in this sense. The equations which follow therefore, treat absorption by an aggregate of nuclei with positive magnetic moments, the results will be equally valid for a negative moment if the $\bar{H}_1$ field precesses about $+z$, but no distinction will be necessary in the experimental situation which uses the oscillating field $H_x = 2H_1 \cos wt$, as both precessing components are present.

It is assumed for simplicity that the sample contains but one magnetic nuclear species, of which there are N per unit volume, and that this nucleus has spin I and magnetic moment gI nuclear magnetons. Although overlapping of two different nuclear resonances will seldom occur because the resonances are generally quite narrow, superposition will adapt the results which follow to any situation.

The vector equation of motion for a single nuclear magnetic moment may be written from Eq.(9) as

$$\frac{d\bar{\mu}}{dt} = g\left(\frac{e}{2Mc}\right) \bar{\mu} \times \bar{H}. \qquad (55)$$

Summing over all the nuclear moments in a unit volume of the sample transforms Eq.(55) into

$$\frac{d\bar{M}}{dt} = \gamma\, \bar{M} \times \bar{H}, \qquad (56)$$

where

$$\gamma = g\left(\frac{e}{2Mc}\right) = \frac{\omega_0}{H_0}. \qquad (57)$$

However, Eq.(56) is correct only if the following assumptions are made:

1. That the changes of orientation of each nucleus are solely due to the presence of the external fields.
   a) The atomic electrons do not cause appreciable fields to act upon the nuclei.
   b) The interaction between neighboring nuclei can be neglected.
   c) The thermal agitation does not essentially affect the nuclei, i.e., the relaxation time is long compared to the considered time intervals.
2. That the external fields are uniform throughout the sample.

Hence Eq.(50) represents but one of several contributions to $d\bar{M}/dt$, other contributions arise from the processes discussed in the previous chapter. For example, the ζ - component of magnetization is proportional to the excess number in the lower energy states, and Eqs. (44) & (46) produce a spin-lattice contribution

$$\frac{dM_z}{dt} = \frac{(M_o - M_z)}{T_1} \quad . \tag{58}$$

The final contribution arises through spin-spin processes, which were found in the previous chapter to destroy phase relationships between the precessing (x- and y-) components of the nuclear magnetic moments. This destruction of the x- and y- components may be expressed by the equations

$$\left.\begin{aligned} \frac{dM_x}{dt} &= \frac{M_x}{T_2} \\ \frac{dM_y}{dt} &= \frac{M_y}{T_2} \quad . \end{aligned}\right\} \tag{59}$$

Integration of each equation in (59) by itself verifies that these components would die out to 1/e of their initial values after time T_2.

Upon evaluating the cross products in Eq.(56) and adding the contributions from Eqs.(58) & (59), one obtains the Bloch equations.

$$\left.\begin{aligned} \frac{dM_x}{dt} &= \gamma\left[M_y H_o + M_z H_1 \sin\omega t\right] - \frac{M_x}{T_2} \\ \frac{dM_y}{dt} &= \gamma\left[M_z H_1 \cos\omega t - M_x H_o\right] - \frac{M_y}{T_2} \\ \frac{dM_z}{dt} &= \gamma\left[-M_x H_1 \sin\omega t - M_y H_1 \cos\omega t\right] + \frac{(M_o - M_z)}{T_1} \end{aligned}\right\} \quad . \tag{60}$$

The resonant absorption phenomenon that is treated here is described largely by a particular solution of Eq.(60) which is obtained in Appendix A. In the absorption experiments one is interested in M_x and M_z since the experimentally applied fields $2\bar{H}_1 \cos \omega t$ and $\bar{H}_0$ are in these directions. One finds,

$$M_x = \tfrac{1}{2} \chi_0 \omega_0 T_2 \frac{(2H_1 \cos \omega t) T_2 (\omega_0 - \omega) + 2H_1 \sin \omega t}{1 + T_2^2 (\omega_0 - \omega)^2 + \gamma^2 H_1^2 T_1 T_2} \tag{61}$$

$$M_z = \chi_0 H_0 \frac{1 + T_2^2 (\omega_0 - \omega)^2}{1 + T_2^2 (\omega_0 - \omega)^2 + \gamma^2 H_1^2 T_1 T_2} \tag{62}$$

Where χ_0 is the Curie susceptibility in Eq.(28).

Comparison of Eq.(61) with Eq.(52) identifies the Bloch susceptibilities as

$$\chi' = \tfrac{1}{2} \chi_0 \omega_0 T_2 \frac{T_2 (\omega_0 - \omega)}{1 + T_2^2 (\omega_0 - \omega)^2 + \gamma^2 H_1^2 T_1 T_2} \tag{63}$$

$$\chi'' = \tfrac{1}{2} \chi_0 \omega_0 T_2 \frac{1}{1 + T_2^2 (\omega_0 - \omega)^2 + \gamma^2 H_1^2 T_1 T_2} \tag{64}$$

Finally the absorption is obtained from Eq.(53) and the above value of χ''

$$A = \omega H_1^2 \chi_0 \frac{\omega_0 T_2}{1 + T_2^2 (\omega_0 - \omega)^2 + \gamma^2 H_1^2 T_1 T_2} \,. \tag{65}$$

The key equation (55) into which Bloch introduced the interactions involving T_1 and T_2 is a classical one, and it may well be asked why it can be applied with such confidence to the small nuclear domain under consideration. In the quantum mechanical formalism, the magnetic moment $\bar{\mu}$ is replaced by an "operator", and a procedure is developed for finding, directly from the operator and the nuclear wave function, the "expectation value" of the quantity the operator represents. The quantum mechanical expression for the time derivative of the magnetic moment operator is identical in form to Eq.(55), $\bar{\mu}$ being replaced by the operator. Upon proceeding to take the expectation value of each number, one alters in no way the form of the equation, which is now satisfied by the expectation value of $\bar{\mu}$. This expectation value corresponds to the observable quantity in an experiment, and therefore, Eq.(55) describes the system no matter how large or small its quantum numbers may be.

The Bloch susceptibilities may be simplified by considering two different physical situations.

a) No saturation effects

b) Saturation effects

a) <u>No saturation effects</u> -- Consider first the situation when

$$s = \gamma^2 H_1^2 T_1 T_2 \ll 1 . \qquad (66)$$

For example, this condition, when applied to the proton resonance in water at 7000 gauss, requires that H_1 be about one milligauss or smaller. The susceptibilities of Eqs.(63) & (64) then reduce to

$$\chi' = \tfrac{1}{2}\chi_0 \omega_0 T_2 \frac{T_2(\omega_0-\omega)}{1+T_2^2(\omega_0-\omega)^2} \qquad (67)$$

$$\chi'' = \tfrac{1}{2}\chi_0 \omega_0 T_2 \frac{1}{1+T_2^2(\omega_0-\omega)^2} \qquad (68)$$

and the absorption is

$$A = 2H_1^2 \omega \chi'' \quad . \qquad (69)$$

The factor ω in Eq.(69) may usually be replaced by ω_0 since the resonance is ordinarily quite narrow compared to the resonance frequency ω_0. Eqs.(67) & (68) are plotted in Fig.(8) against an abscissa $\epsilon = T_2(\omega_0-\omega)$. The resonant character of the absorption is apparent, maximum absorption occurring at the Larmor frequency. Further, the half-width at half maximum intensity occurs when

$$T_2 |\omega_0-\omega|^{1/2} = 1 \qquad (70)$$

and thus $1/T_2$ is the half-width expressed as an angular frequency. The qualitative considerations of Chapter Four are borne out: spin-spin processes fix the line width in a perfectly homogeneous field.

The Bloch susceptibilities have the so-called Lorentz shape[17] which was first obtained in the simple classical analysis of radiation by a damped oscillator.

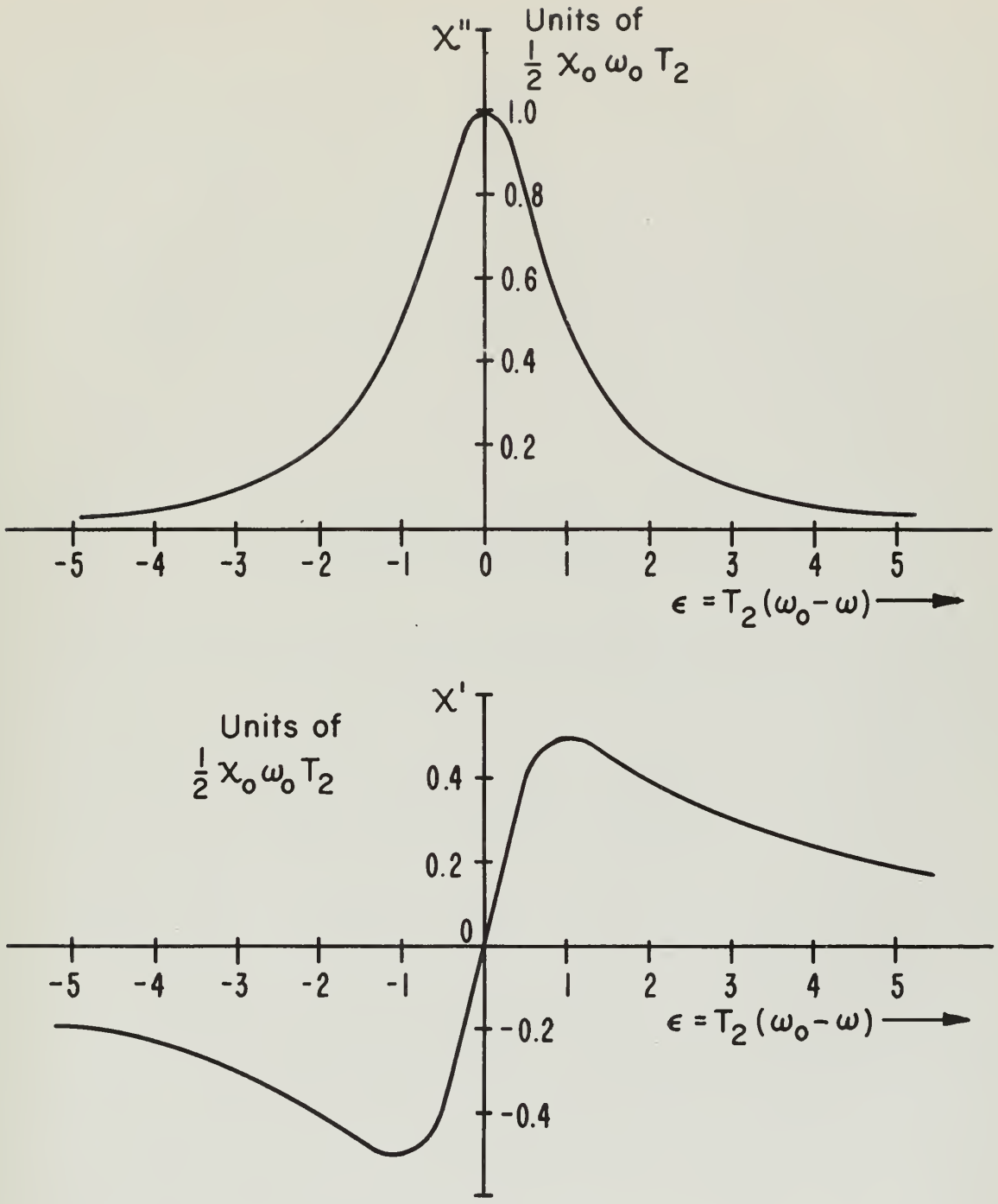


Fig. 8

The Bloch nuclear susceptibilities plotted against the dimensionless variable $\epsilon = T_2(\omega_0 - \omega)$. These graphs apply to conditions of negligible saturation

b) Saturation effects -- The restriction of Eq.(66) is now removed and H_1 is allowed to increase until $\gamma^2 H_1^2 T_1 T_2$ has a value of the order of unity. Under this condition, the nuclear spin system is said to be saturated, that is, it is soaking up radiofrequency energy to such an extent that the relaxation processes are unable to keep it at the lattice temperature. One can observe this directly from the expression (62) for M_z if χ_0 is replaced by its value in Eq.(28). The maximum value of M_z is then

$$M_{z(\omega=\omega_0)} = \frac{N g^2 \mu_0^2 I(I+1) H_0}{3kT(1+\gamma^2 H_1^2 T_1 T_2)} . \qquad (71)$$

Eq.(71) has a form that suggests the definition of an effective spin temperature

$$T_s^{eff} = T\left(1+\gamma^2 H_1^2 T_1 T_2\right), \qquad (72)$$

since, if the constant field H_0 alone were applied at a real temperature equal to T_s^{eff}, Eq.(71) would give the equilibrium value of M_z which would arise. Thus the excess population in the lower energy states is reduced when $\gamma^2 H_1^2 T_1 T_2$ is no longer negligible compared to unity. The absorption is also affected by saturation. Although the expression (69) for A increases directly with H_1^2 the general expression (65) approaches the constant value:

$$A_{(sat)} = \frac{\omega \omega_0 \chi_0}{\gamma^2 T_1} \qquad (73)$$

as H_1^2 is increased indefinitely.

CHAPTER 6

POSSIBILITIES AS SPACE REFERENCE

In the previous chapters both the classical and microscopic study of nuclear resonance have been treated in sufficient detail to enable a discussion of the results on an intuitive basis. During resonance the spin system may be characterized by a single magnetic moment $\bar{M}$, per unit volume precessing about an external magnetic field $\bar{H}$. If one chooses a sample where the relaxation time T_1 is long then the motion may be expressed by the equation

$$\frac{d\bar{M}}{dt} = \gamma \left(\bar{M} \times \bar{H} \right)$$

where γ is the gyromagnetic ratio. A special solution of this equation exists where the z component of $\bar{M}$ is constant, i.e., $M_z = M \cdot \cos \theta$, where θ is the angle between $\bar{H}$ and $\bar{M}$. Hence, since the resultant angular momentum vector of the spin system $\bar{A}$ is related to $\bar{M}$ by

$$\bar{M} = \gamma \bar{A}$$

one would expect the z component of $\bar{A}$ likewise to remain constant in magnitude. It would seem therefore that one could indicate the

direction of this angular momentum with respect to inertial space simply by observing what the direction of the field $\bar{H}$ is when resonant conditions are established according to the expression

$$\omega_0 = \gamma H_0$$

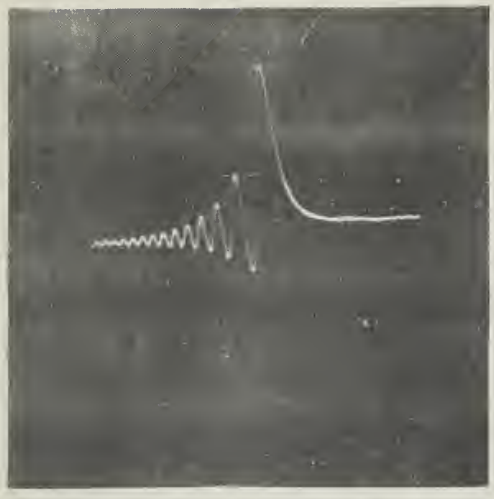
where the subscript 0 denotes resonant values.

However, this is not the case since resonance can be observed only when an external constant magnetic field is applied, thus precession will take place only about the direction of this external field. Hence the direction of the associated angular momentum will be conserved **only** with respect to the direction of the external field and not with respect to inertial space. The angular momentum property of the nucleus, $I\hbar$, contained in the gyromagnetic ratio

$$\gamma = \frac{\mu}{I\hbar} = 2.66 \times 10^4 \text{ c.g.s. (for protons)}$$

can only affect the magnitude of the resonance conditions, i.e., it can only change the magnitude of ω_0 or H_0, but it cannot manifest itself in the form of a direction independent of $\bar{\mu}$. This argument corresponds to the energy considerations discussed in Chapter Five.

Therefore, if the external field were suddenly removed, the precessing nuclei would, after a transient,[18] precess about the strongest field available, namely the earth's field, until the energy of the system is diminished through the thermal agitation.



Proton resonance in enriched mineral oil. H_o = 4,220 gauss $\boxed{2\pi f_o = \gamma H_o}$, f_o = 20 megacycles f_o is modulated by 30 cps, Wiggles due to non-adiabatic variation of f_o, Sweep is from right to left.
(Courtesy of Chemistry Dept.)

Fig. 9

This transient is illustrated in Fig.(9) which was photograped at the Department of Chemistry resonance apparatus.

Cursory investigations have been made with regard to other possible applications of the resonance phenomena. Suggestions were made to use nuclear resonance principles in high precision resolvers. However this implies the use of electromagnets so that the necessary fields may be varied by varying the coil current according to the values of the vector magnitudes and directions which are to be summed. The electrical power necessary for proper operation and the bulk of the proposed apparatus appear to be prohibitively large to be practical for airborne operation.

To be sure, nuclear resonance can be and has been used to accurately calibrate[19][24] the value of magnetic field intensities.

Reference (19) reports an accuracy of one part per 40,000.

Despite the apparent negative results of this paper, the writer feels that since, in the principle of nuclear magnetic resonance, there resides a means of obtaining measurements of high precision with relatively simple equipment the subject should be further investigated. (See additional Bibliography in Appendix D for feasible engineering applications.)

APPENDIX A

To help obtain the particular solution of the Bloch equations, define the complex numbers

$$\mathcal{M}_+ = M_x + i M_y$$
$$\mathcal{M}_- = M_x - i M_y$$

first add i times the second equation of (60) to the first, then subtract i times the second from the first, obtaining

$$d\mathcal{M}_+/dt = \gamma\left[-iH_0\mathcal{M}_+ + iH_1\mathcal{M}_3 e^{-i\omega t}\right] - \mathcal{M}_+/T_2 \qquad \text{(A-1)}$$

$$d\mathcal{M}_-/dt = \gamma\left[iH_0\mathcal{M}_- - iH_1\mathcal{M}_3 e^{i\omega t}\right] - \mathcal{M}_-/T_2 \qquad \text{(A-2)}$$

The time dependence is removed by letting

$$\left.\begin{aligned}\mathcal{M}_+ &= e^{-i\omega t}\,\eta_+ \\ \mathcal{M}_- &= e^{i\omega t}\,\eta_-\end{aligned}\right\} \qquad \text{(A-3)}$$

so that Eqs.(A-1) & (A-2) become, after substituting $\omega_0 = \gamma H_0$,

$$\left.\begin{aligned}i\omega\eta_+ &= i\omega_0\eta_+ - i\omega_0(H_1/H_0)\mathcal{M}_3 + \eta_+/T_2 \\ i\omega\eta_- &= i\omega_0\eta_- - i\omega_0(H_1/H_0)\mathcal{M}_3 - \eta_-/T_2\end{aligned}\right\} \qquad \text{(A-4)}$$

Eqs.(A-4) yield N_+ and N_-:

$$\left.\begin{aligned} \eta_+ &= \frac{\omega_0 (H_1/H_0)\, \eta_z}{\omega_0 - \omega - i/T_2} \\ \eta_- &= \frac{\omega_0 (H_1/H_0)\, \eta_z}{\omega_0 - \omega + i/T_2} \end{aligned}\right\} \qquad \text{(A-5)}$$

To evaluate η_z one requires the third equation of (60). A solution is sought which is characterized by a steady-state absorption, and it will be assumed that η_z is time independent. This assumption is not so restrictive as to require that the spin and lattice temperatures be equal, but merely requires that the spin system reach equilibrium determined by the inflow of r-f energy, the relaxation times, and the lattice temperature. This equilibrium state may correspond to a spin temperature appreciably higher than the lattice temperature.

The assumption $d\eta_z/dt = 0$, combines with the identity

$$M_x \sin\omega t + M_y \cos\omega t = \left(\frac{1}{2i}\right)\left(\eta_+ e^{i\omega t} - \eta_- e^{-i\omega t}\right)$$

to yield from Eq.(60) that

$$\frac{\gamma H_1}{2i}\left[\eta_+ e^{i\omega t} - \eta_- e^{-i\omega t}\right] = \frac{\eta_z - M_0}{T_1} \qquad \text{(A-6)}$$

which on further rearranging becomes

$$\frac{M_0 - m_z}{T_1} = \omega_0 \left(\frac{H_1}{H_0}\right) \left[\frac{\eta_+ - \eta_-}{2i}\right] . \qquad \text{(A-7)}$$

The bracket of Eq.(A-7) is found directly from Eq.(A-5). Since the bracket is real, m_z may be replaced by M_z and, upon solving the resultant expression for M_z one obtains

$$M_z = \chi_0 H_0 \frac{(\omega_0 - \omega)^2 + 1/T_2^2}{(\omega_0 - \omega)^2 + (1/T_2^2) + (\gamma^2 H_1^2 T_1 / T_2)} . \qquad \text{(A-8)}$$

The quantity M_x may be obtained from

$$M_x = \frac{1}{2}(m_+ + m_-) = \frac{1}{2}\left[\eta_+ e^{-i\omega t} + \eta_- e^{i\omega t}\right]$$

and Eq.(A-5) as

$$M_x = \frac{1}{2}\omega_0 \left(\frac{H_1}{H_0}\right) m_z \left[\frac{e^{-i\omega t}}{\omega_0 - \omega - i/T_2} + \frac{e^{i\omega t}}{\omega_0 - \omega + i/T_2}\right] \qquad \text{(A-9)}$$

Since M_z is real and the terms in the brackets are complex conjugates, the expression (A-9) is also real and

$$M_x = \frac{1}{2}\omega_0 \chi_0 T_2 \left[\frac{(2H_1 \cos\omega t) T_2 (\omega_0 - \omega) + 2H_1 \sin\omega t}{1 + T_2^2(\omega_0 - \omega)^2 + \gamma^2 H_1^2 T_1 T_2}\right] . \qquad \text{(A-10)}$$

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APPENDIX C

GLOSSARY

$\bar{\mu}$ = Magnetic moment vector

$\bar{p}$ = Angular momentum vector

c = Velocity of light in vacuum

M = Mass of proton

e = Charge on the proton

g = Nuclear g-factor (dimensionless)

$\hbar$ = $(2\pi)^{-1}$ times the planck constant = $\frac{1}{2\pi}$ $(6.624 \times 10^{-27}$ erg-sec)

$\bar{H}$ = Magnetic field

$\bar{I}$ = Nuclear spin vector (dimensionless)

m = Magnetic quantum number (dimensionless)

I = Nuclear Spin (maximum value of m)

$\bar{L}$ = Torque vector

ω_0 = Angular frequency of Larmor precession

$U(m)$ = Zeeman energy of a magnetic moment in state m

μ_0 = $e\hbar/(2Mc)$ = Nuclear magneton

μ = gI = dimensionless number of nuclear magnetons: "The nuclear magnetic moment"

$\bar{B}$ = Magnetic induction vector

$\bar{M}$ = Volume density of magnetization

χ = Magnetic susceptibility (dimensionless)

N = Number of nuclear magnetic moments per unit volume

k = Boltzmann constant = 1.38×10^{-16} erg/deg

T = Absolute temperature, usually of the lattice

$N(m)$ = Number of nuclei per unit volume in state m

χ_o = Nuclear Curie susceptibility

ω = Angular frequency of incident radiation

$\bar{H}_1$ = Rotating magnetic field

$\bar{H}_0$ = Constant magnetic field vector

$P(m \rightarrow m^1)$ = Transition probability per unit time

ν = Frequency of radiation

$\rho(\nu)$ = Energy density of radiation at frequency ν

$c(m \rightarrow m^1)$ Absolute transition probability

T_1 = Spin-lattice relaxation time

T_s = Temperature of nuclear spin system

$W(p \rightarrow q)$ Total transition probability per unit time after detailed balancing

n = Excess of nuclei per unit volume in lower Zeeman state (for I= 1/2)

n_0 = Equilibrium value of n for $T_s = T$

H_{loc} = Magnetic field produced at a lattice point by neighboring nuclear moments

A = Energy absorbed per second per unit volume

χ', χ'' = Real and imaginary parts of $\chi = \chi' - i\chi''$

M_0 = Equilibrium value of z - component of nuclear magnetization

T_2 = Time for a freely precessing component of nuclear magnetization to fall to e^{-1} of its value; inverse measure of line width

γ = $ge/(2Mc)$ = ratio of angular Larmor frequency to magnetic field (gyromagnetic ratio)

ϵ = $T_2(\omega_0 - \omega)$ = dimensionless variable

$s = \gamma^2 H_1^2 T_1 T_2$ = saturation factor

APPENDIX D

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